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STABLE SOLUTIONS OF METAL CHELATES, METHOD FOR THEIR PREPARATION AND THEIR USE AS TRACE ELEMENT FERTILIZERS

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STABLE SOLUTIONS OF METAL CHELATES, METHOD FOR THEIR PREPARATION AND THEIR USE AS TRACE ELEMENT FERTILIZERS

[Stabile Lösungen von Metallchelaten, Verfahren zu ihrer Herstellung und ihre Verwendung als Spurenelementdünger]

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This invention concerns stable solutions of metal chelates, a method for producing them and their use as trace element fertilizers. The metals iron, manganese [sic]* can be present in the trace element fertilizers in accordance with the invention, with one or more N-carboxyalkylamino acids, individually, or in combination with several trace elements. /2*

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* [Numbers in the margin indicate pagination of the original foreign language text.]

The solutions in accordance with the invention can contain one or more of the said trace elements in chelated form; moreover, they can contain boron, as a soluble borate or boric acid, and molybdenum, in the form of water-soluble molybdates.

Normal plant development requires a sufficient supply of primary nutrients like nitrogen, phosphorus, potassium, calcium and magnesium, but it also requires trace nutrients like iron, manganese, boron, molybdenum, copper, zinc and cobalt, to name just a few.

If one of these elements is not supplied or if the supply is insufficient, deficiency diseases will arise in the plant.

Very often deficiency diseases also result because of insufficient availability of the trace elements. Insufficient availability for plants can occur, for example, if the trace elements are in the form of sparingly soluble compounds, especially as hydroxides, oxides or phosphates.

For example, chlorosis disease caused by a lack of iron is well known. It can be remedied by supplying suitable soluble iron compounds. Iron chelate complexes of aminocarboxylic acids, especially ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), N-hydroxyethylethylenediaminetriacetic acid (HEEDTA) and ethylenediaminedi-(o-hydroxyphenylacetic acid) (EDDHA), in particular, have proven themselves here.

Supplying soluble nonchelated iron compounds is not suitable for remedying chlorisis for a long time. The iron ions are converted to insoluble iron hydroxide or iron phosphate, especially at a high pH value, and cannot be absorbed by the plants.

For these reasons, the said chelate complexes are used for treatment and prevention of trace element deficiency phenomena and to increase yields.

The fertilization chiefly takes place with solid or paste-like products.

For some time now, growing plants in a substrate culture (hydroculture) has become increasingly important, especially for vegetables and flowers. With this growing method the plants are cultivated on suitable porous materials, for example, rockwool, porous clay or foamed plastics, while supplying the primary and trace nutrients that are required for growth.

The nutrients are continuously supplied to the plants in dissolved form. In order to guarantee an optimum supply of nutrients, automatic dispensing stations have been developed, which put together a nutrient supply matched to each plant variety from different stork solutions and transport the nutrients to the plants via appropriate transport devices.

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* [From the abstract and the claims it would appear that the phrase "copper, zinc or cobalt" has been omitted here...translator.]

A prerequisite for trouble-free operation of such dispensing stations is the use of stable and solids-free stock solutions. Even negligible amounts of insoluble components can lead to plugging of the dispensing devices and for this reason are prohibitive for this kind of delivery. Trace element fertilizers can be prepared in various ways:

According to DE-C2 313 921 multiple trace element fertilizers can be obtained by mixing simple metal salts (nitrates, sulfates, chlorides) with alkali salts of the complexing aminocarboxylic acids. Disadvantages of these products are their tendency to demix as well as unavoidable caking caused by the water of crystallization that is introduced. Moreover, these products are not water-soluble without residues.

DE-B 2 846 832 describes the preparation of paste products from metal sulfates, aminocarboxylic acids and polyethylene glycols.

According to DE-A 3 325 059 metal chelates can be obtained in granular form through the addition of paraffins, fatty alcohols or fatty acids.

These granulates, like the described paste products, cannot be used in substrate cultures because they have insufficient solubility. Products of this kind can only be used successfully in soil fertilization.

EP-A 53 246 describes the preparation of solid multiple trace element fertilizers by mixing the simple metal salts with aminocarboxylic acids or the alkali or ammonium salts of aminocarboxylic acids and then drying the resulting mixture. These products are also not water-soluble without residue.

Moreover, it is known that trace element solutions can be prepared from the chelate complexes of the individual components by mixing them together (JA 58 204 892). This method is very expensive, since the individual components must first be prepared in separate operations. /3

Stable zinc EDTA solutions are described in US patent 4,399,070, and stable manganese chelate solutions are described in US patent 4,322,361. However, these methods are limited to the preparation of zinc or manganese chelate solutions. Iron, copper and cobalt chelate solutions cannot be obtained by these methods, nor can liquid multiple trace element fertilizers.

Solid or paste products that are prepared by the methods described above are unsuitable for use in substrate culture for several reasons:

1. The products have to be dissolved before use. This requires additional technical equipment. Due to the poor solubility, they also have to be filtered.

2. The solutions thus prepared have a low usage concentration, which necessitates the installation of large supply vessels.

3. The solutions thus prepared are not storage stable. Especially at low temperatures, there can be undesired formation of crystals with the consequence that plugging of the automatic dispensing devices will occur.

4. The metal chelates that can be obtained by the prior art do offer higher availability of metal ions for plants than do the nonchelated metal salts. However, under unfavorable conditions, they do have limitations. For instance, the availability of iron for plants, for example, when using iron-EDTA chelates in nutrient solutions at high pH values, still amounts to only a fraction of the iron that is used.

For this reason there was the task of developing liquid trace element fertilizers that guarantee high availability of the trace elements in nutrient solutions even at high pH values, that have a high active agent concentration and that are storage-stable even under unfavorable ambient conditions and do not have a tendency to crystallize.

This task is solved in accordance with the invention by the fact that solutions of the sodium, potassium or ammonium salts of commercial aminocarboxylic acids (for example, ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), N-hydroxyethylethylenediaminetriacetic acid (HEEDTA), ethylenediaminedi-(o-hydroxyphenylacetic acid) (EDDHA)) are reacted with the nitrate salts of the corresponding trace elements. In doing so, the trace element complex salts (chelates) or the next alkali, or ammonium, trace element complex salts of the aminocarboxylic acids are formed, in addition to alkali/ammonium nitrate.

The metal:chelating agent mol ratio is at least 0.5:1 and at most 1:0.2; preferably it is between 0.8:1 and 2.5:1.

The solutions in accordance with the invention contain one or more of the trace elements iron, copper, cobalt, manganese or zinc and one or more complexing agents, for example, nitrilotriacetic acid (NTA), EDTA, DTPA, HEEDTA, EDDHA.

For example, the solutions of the sodium salts of EDTA, DTPA or HEEDTA can be reacted at room temperature with nitrates of iron, copper, manganese, zinc or cobalt that are free of water or contain water of crystallization. To accelerate the dissolving process and the complexing, the reacting components can optionally be heated. The pH of the resulting chelate solutions can optionally be corrected by adding acids or bases if it deviates from the preferred range of pH 4-8. Possibilities as acids for this are mineral acids, for example, nitric acid, hydrochloric acid, phosphoric acid, as well as the free aminocarboxylic acids, for example, EDTA. Alkali oxides, hydroxides, carbonates, ammonia (gaseous or aqueous solution) and the alkali/ammonium salts of the aminocarboxylic acids can be used as bases.

In addition, the solutions in accordance with the invention can be prepared from the free aminocarboxylic acids and metal nitrates with the addition of suitable bases.

The active agent content of the solutions in accordance with the invention can be increased by removing water by distillation. The solids content of the solutions should not exceed a total of 60%. Precipitations can occur at high concentrations.

The storage stability is an important criterion for the usability of the trace element solutions.

The storage stability of the solutions in accordance with the invention was tested according to criteria that are similar to practical conditions:

Storage at +50°C
Storage at -10°C
Storage at alternating temperatures (-10°C to +30°C).

Storage stability is indicated if under the said conditions, neither crystallization nor sedimentation takes place after three months.

The high solubility of the alkali/ammonium nitrate causes the solutions with high active agent contents that are prepared in this way not to crystallize even at temperatures under 0°C. /4

Another advantage of the solutions in accordance with the invention is that the sulfate ions of the traditional trace element fertilizers, which are phytotoxic at higher levels, are replaced by the nitrate ions, which are well tolerated by plants.

The trace element solutions in accordance with the invention can be used either directly or after being diluted with water, or before application can be mixed with the primary fertilizers that are necessary for plant nutrition and used as a combined complete fertilizer. Through suitable mixture ratios one can in this way prepare a solution that is matched to the relevant plant and substrate conditions.

The availability of the trace element ions is generally higher in chelate solutions than in solutions that contain only the simple metal salts.

High availability is especially important in the case of iron, since immobilization through precipitation of the iron ions or through adsorption of the iron chelates can occur to a far greater extent than with other trace elements. This immobilization is highly dependent on the pH.

While iron is chiefly in divalent form in commercial chelates, the iron chelate solutions in accordance with the invention contain trivalent iron.

The iron chelate solutions in accordance with the invention also have higher stability at high pH values than nonchelated iron compounds or commercial solid iron chelates do.

The higher stability occurs both in the concentrated stock solutions and in the presence of the primary and trace nutrients that are important for plant nutrition.

This is demonstrated by the tests described below.

Experiments

To a nutrient solution that contains 10.5 mmol/L nitrate,
1.5 mmol/L phosphate

2.5 mmol/L sulfate
0.5 mmol/L ammonium
7.0 mmol/L potassium
3.8 mmol/L calcium
1.0 mmol/L magnesium
10.0 mmol/L manganese
4.0 mmol/L zinc
0.5 µmol/L copper
0.5 µmol/L molybdenum and
20.0 µmol/L borate ion

are added 50 ppm each to iron ions in the form of iron II sulfate, commercial iron II DPTA and iron I HEEDTA chelates and the iron III DTPA and iron III HEEDTA chelates in accordance with the invention. The pH of the solutions is adjusted to values from 5.0 to 9.0 using ammonia or phosphoric acid. The mixtures are filtered after standing for three days in the light, and the amount of available iron in the filtrates is determined.

Amount of available (soluble) iron, %*

pH-Wert	Fe-II-SO$_4$ 7 H$_2$O	Fe-II-DTPA	Fe-III-DTPA (Beispiel 1)	Fe-II-HEEDTA	Fe-III-HEEDTA (Beispiel 2)
5,0	98	100	100	98	100
6,0	74	100	100	85	96
7,0	42	95	98	81	92
8,0	5	90	88	71	81
9,0	1	60	63	48	79

Key		
	1	pH value
	2	(Example 1)
	3	(Example 2)

Solutions of the chelate complexes of trace elements in accordance with the invention can generally be used for plant nutrition, especially where the use of liquid products is superior to the use of solid products.

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* [Note: Commas in numbers in table indicate decimal place.]

For example, the hydroculture or substrate culture of flower and vegetable plants are preferred field of application of the solutions in accordance with the invention.

However, the solutions in accordance with the invention can also be used with advantage for leaf fertilizing in vegetable growing and vineyards. If the solutions in accordance with the invention are mixed with pesticides, moreover, the number of work operations can be reduced by comparison with the separate application of these components.

The following examples serve for more detailed illustration of the preparation of the solutions in accordance with the invention.

Example 1

243 g iron III nitrate nonahydrate are added while stirring to 757 g of a 40% solution of DTPA pentasodium salt, and the solution is briefly heated to boiling. 1000 g of a clear brown solution are obtained.

pH: 6.0

Fe content: 3.4%

The solution is storage-stable.

Removing water by distillation produces solutions containing 3.5 to 5.0% Fe. These solutions are also storage-stable.

Example 2

320 g iron III nitrate nonahydrate are added while stirring to 680 g of a 40% solution of HEEDTA trisodium salt, and the solution is briefly heated to boiling. The pH is adjusted to 6.0 with ammonia. A clear reddish brown solution is obtained.

Fe content: 4.5%

The solution is storage-stable.

Example 3

193 g copper II nitrate trihydrate are added while stirring to 688 g of a 40% solution of HEEDTA trisodium salt. The pH is adjusted to 6.0 with 65% HNO_3. A clear blue solution is obtained.

Cu content: 5.7%

The solution is storage-stable.

Example 4

233 g cobalt II nitrate hexahydrate are added while stirring to 688 g of a 40% solution of HEEDTA trisodium salt and briefly heated to 100°C. The pH is adjusted to 6.0 with 65% HNO_3. A clear violet solution is obtained.

Cu content: 5.1%

The solution is storage-stable.

Example 5 /6

291 g cobalt II nitrate hexahydrate are added while stirring to 503 g of a 40% solution of DTPA pentasodium salt. A clear violet solution is obtained.

pH: 7.2

Co content: 7.4%

The solution is storage-stable.

Example 6

334 g zinc nitrate hexahydrate are added while stirring to 566 g of a 40% solution of DTPA pentasodium salt. The pH is adjusted to 5.2 with 65% HNO_3. A clear colorless solution is obtained.

Zn content: 8.7%

The solution is storage-stable.

Example 7

14.9 g zinc nitrate hexahydrate, 32.6 g copper II nitrate trihydrate, 107.1 g iron III nitrate nonahydrate and 31.4 g manganese II nitrate tetrahydrate are added in succession while stirring to 723 g of a 40% solution of DTPA pentasodium salt. The mixture is boiled for two hours. The pH is adjusted to 6.5 with 65% HNO_3. A dark green clear solution is obtained.

Zn: 0.35%
Cu: 0.95%
Fe: 1.63%
Mn: 0.75%

The solution is storage-stable.

Example 8

300 g manganese II nitrate tetrahydrate are added while stirring to a mixture of 206 g of a 40% solution of HEEDTA trisodium salt, 300 g of a 40% solution of DTPA pentasodium salt,

210 g EDTA and 80 g water. The mixture is boiled for one hour. A clear brownish solution is obtained.

pH:	4.8
Mn content:	6.0%

The solution is storage-stable.

Example 9

310 g 50% sodium hydroxide and 291 g cobalt II nitrate hexahydrate are added in succession while stirring to a slurry of 292 g EDTA acid in 340 g water. A clear violet solution is obtained.

pH: 6.4
Co content: 4.7%
The solution is storage-stable.

Example 10

290 g 25% ammonia solution and 242 g copper II nitrate trihydrate are added in succession while stirring to a slurry of 292 g EDTA acid in 390 g water. A clear dark blue solution is obtained.

pH: 6
Cu content: 5.2%
The solution is storage-stable.

Example 11

185 g iron III nitrate nonahydrate are added to 1197 g of a 40% solution of DTPA pentasodium salt, and the mixture is heated to 80°C for 15 min. After cooling to 25°C, 55 g manganese II nitrate tetrahydrate, 22 g zinc nitrate hexahydrate, 49 g copper II nitrate trihydrate, 37 g boric acid and 50 g sodium molybdate dihydrate are added in succession. The pH is adjusted to 6.8 with 65% nitric acid.

A clear dark green solution is obtained.

Fe content:	1.6%
Mn content:	0.8%
Zn content:	0.3%
Cu content:	0.8%
B content:	0.4%
Mo content:	1.3%

/7

The solution is storage-stable.

Claims

1. Storage-stable aqueous solutions that contain chelate complexes of the metals iron, manganese, copper, zinc or cobalt with aminocarboxylic acids as chelating agents and that ensure high availability of the metal ions to plants when used as trace element fertilizers, even in the presence of the primary nutrients, characterized by the fact that nitrate salts of the corresponding metal ions are mixed in an aqueous solution with the chelating agents and the pH value of the solution is 4 to 8.

2. Solutions as in Claim 1 that contain NTA, EDTA, DTPA, HEEDTA and/or EDDHA individually or in combination as chelating agents.

3. Solutions as in Claims 1-2 characterized by the fact that the mol ratio of metals to chelating agents is at least 0.5:1, at most 1:0.2, preferably 0.8:1-1.2:1.

4. Solutions as in Claims 1-3, characterized by the fact that in addition to the chelate complexes, boron as boric acid or borate and molybdenum as alkali or ammonium molybdate are also contained in them.

5. A method for preparation of solutions as in Claim 1, characterized by the fact that solutions of the sodium, potassium or ammonium salts of the aminocarboxylic acids that are used as chelating agents are reacted with nitrates of the metals indicated in Claim 1 that are water free or that contain water of crystallization and the pH of the resulting solutions is optionally adjusted to a value between 4 and 8 through the addition of acids or bases.

6. A method as in Claim 5, characterized by the fact that instead of the alkali or ammonium salts of the aminocarboxylic acids, the free acids are reacted in the presence of suitable bases, above all, alkali oxides, hydroxides and carbonates as well as ammonia in gaseous form or as an aqueous solution.

7. The use of the solutions as in Claims 1-6 for trace element fertilization in hydro/substrate culture and as a leaf fertilizer.

European
Patent Office

Application Number
EP 86 10 2425

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.^{4})
A	US-A-3 767 689 (T. DONOVAN) * Column 1, lines 45-71 *	1	C 05 D 9/02 C 07 C 101/28
A	US-A-3 758 540 (A. MARTELL) * Column 3, lines 1-7 *	1	
P,X	US-A-4 588 145 (N. SMITH) * Column 2, lines 21-24 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.^{4})
			C 05 D C 05 G C 07 C

The present search report has been drawn up for all claims.

Place of search	Date of completion of the search	Examiner
The Hague	September 10, 1986	J.P.M. Verhoest

CATEGORY OF CITED DOCUMENTS

X: Particularly relevant if taken alone.
Y: Particularly relevant if combined with another document of the same category.
A: Technological background.
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T: Theory or principle underlying the invention.
E: Earlier patent document, but published on, or after the filing date.
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